

# SYMMETRIES IN NUCLEAR, ATOMIC AND MOLECULAR SPECTROSCOPY<sup>1</sup>

dedicated to the memory of Alain Partensky

**Maurice Kibler**

Institut de Physique Nucléaire de Lyon, IN2P3-CNRS et Université Claude Bernard  
43 boulevard du 11 novembre 1918, F-69622 Villeurbanne Cedex, France

*Abstract.* Contents : How to introduce groups and chains of groups in nuclear, atomic and molecular physics ? Some tools for connecting group theory and quantum mechanics (Wigner's theorem, Wigner-Eckart's theorem, Racah's lemma). Philosophy of some qualitative and quantitative applications to spectroscopy.

---

<sup>1</sup>Lecture presented at the fifth *Séminaire Rhodanien de Physique* 'Sur les symétries en physique' held at the Domaine de Buffières (Dolomieu, France, 17 – 21 March 1997). To be published in **Symmetries in Physics**, eds. F. Gieres, M. Kibler, C. Lucchesi and O. Piguet (Editions Frontières, Paris, 1998). An extended version of this paper is under preparation. The interested reader may contact the author for any comment, criticism and/or suggestion.

# SYMMETRIES IN NUCLEAR, ATOMIC AND MOLECULAR SPECTROSCOPY

dedicated to the memory of Alain Partensky

**Maurice Kibler**

Institut de Physique Nucléaire de Lyon, IN2P3-CNRS et Université Claude Bernard  
43 boulevard du 11 novembre 1918, F-69622 Villeurbanne Cedex, France

*Abstract.* Contents : How to introduce groups and chains of groups in nuclear, atomic and molecular physics ? Some tools for connecting group theory and quantum mechanics (Wigner's theorem, Wigner-Eckart's theorem, Racah's lemma). Philosophy of some qualitative and quantitative applications to spectroscopy.

## 1 Introduction

This lecture is not a long and complete development on the use of symmetries (via group theory) in nuclear, atomic and molecular physics. It rather addresses the three following questions.

1. How the structures of group and of chain of groups enter nuclear, atomic and molecular spectroscopy ?

2. How these structures can be exploited, in a quantum-mechanical framework, in the problems of state labelling and (external<sup>2</sup>) symmetry breaking ?

---

<sup>2</sup>We are not concerned here with the concept of spontaneous symmetry breaking which is familiar in gauge theories of elementary particle physics. Let us however mention that this concept also occurs in nuclear physics (e.g., transition spherical nucleus  $\rightarrow$  deformed nucleus) and in molecular physics (e.g., Jahn-Teller effect).

**3.** How it is possible to associate a Wigner-Racah algebra to a group or a chain of groups for making easier the calculation of quantum-mechanical matrix elements ?

We shall be mainly concerned in this lecture with the use of symmetries, via group theory, for classifying wavefunctions and interactions and for calculating matrix elements. The group theory to be used is along the lines developed by G. Frobenius, I. Schur, S. Lie, E. Cartan, H. Weyl, E.P. Wigner and G. Racah. In this respect, the reader should note how Wigner's and Racah's legacies are important for the applications of symmetries in nuclear, atomic, molecular and condensed matter physics. We shall not consider here external (i.e., Lorentzian) symmetries and internal (i.e., gauge) symmetries which are of paramount importance in elementary particle physics. The latter symmetries shall be investigated in other lectures. It is enough to underline here the importance of the gauge symmetry principle for generating (electroweak and strong) interactions and of the extended space-time symmetries for understanding the unification of external and internal symmetries through supersymmetry.

Generally speaking, the emphasis in this lecture is on the philosophy rather than on detailed calculations. However, four basic theorems as well as the Wigner-Racah algebra for a finite or compact group are presented in a linear and pedagogical way. Numerous examples illustrate the general ideas and a (necessarily incomplete) list of applications closes this lecture.

## **2 Introducing Groups and Chains of Groups**

The introduction of the structure of group in connection with the concept of conservation laws is familiar to the physicist. If a classical or quantum physical system presents symmetries, then it is often possible to associate a Lie group, say  $G$ , to this system. This group describes some invariance of the physical system. As a result, there exist  $r$  conserved quantities or charges if  $r$  is the order, i.e., the number of essential parameters, of the invariance group  $G$  (cf., Noether's theorem). In short, we have the sequence

$$\text{symmetries} \rightarrow \text{group} \rightarrow \text{invariance} \rightarrow \text{conservation laws}$$

that is of special relevance for gauge theories and that will be discussed in some of the other lectures.

In spectroscopy, groups may be introduced in two complementary ways (viz., as symmetry groups and as classification groups) that we shall discuss in turn

with examples. Most of the examples shall be worked out again in the other sections.

**1. As symmetry groups.** If a Hamiltonian  $H$  exhibits symmetries, we can introduce a (discrete or continuous) symmetry group  $G$ . The association of a group to a Hamiltonian is often a transcription of Curie's principle in its familiar formulation : 'The effects have the same symmetries as the causes'. The group  $G$  is in general a subgroup of the most general group that leaves the Hamiltonian invariant. According to Wigner's theorem (to be proven in Section 3.1), it is then possible to classify the state vectors of  $H$  and the interactions which occur besides  $H$  by means of the irreducible representations of  $G$ . A *symmetry* or *invariance* group is thus a *classification* group too. The appropriate sequence is now

$$\text{symmetries} \rightarrow \text{group} \rightarrow \text{invariance} \rightarrow \text{conserved quantum numbers}$$

where the notion of 'conserved quantum numbers' or 'good quantum numbers' arises from the fact that the Hamiltonian  $H$ , invariant under  $G$ , cannot connect state vectors labelled by different irreducible representations of  $G$  (this result shall be proven in Section 4.7).

**Example 1.** The Hamiltonian for a  $N$ -body system comprising  $N$  identical particles is invariant under the symmetric group  $S_N$ . The wavefunctions for this system have thus well-defined transformation properties under the operations of  $S_N$ . We know that Physics selects the antisymmetric and the symmetric (with respect to the permutation of two particles) wavefunctions for fermions and bosons, respectively.

**Example 2.** The geometrical symmetry group of a (nonrelativistic) Hamiltonian  $H = T + V$  is commonly the discrete or continuous group that leaves the potential  $V$  invariant.

For instance, a complex atom is rotationally invariant and its geometrical symmetry group is the full rotation group. This group is isomorphic to the orthogonal group  $O(3)$  and we say that the geometrical symmetry group of the atom is  $O(3)$ . The invariance of ( $V$  and)  $H$  under  $O(3)$  ensures that the eigenfunctions of  $H$  behave in a well-defined way under the elements of  $O(3)$ .

As a second illustration, an ion embedded in a molecular environment and its environment possess a finite symmetry. This is the case for the complex ion  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  for which the six dipoles  $\text{H}_2\text{O}$  are located at the vertices of a (slightly deformed) octahedra and the central cation  $\text{Ti}^{3+}$  occupies the center of the octahedra. This complex ion is thus (almost) invariant under the octahedral

group  $O_h$ . The same invariance applies to the potential in the Hamiltonian  $H$  of the ion  $\text{Ti}^{3+}$ ; in first approximation, the geometrical symmetry group of  $H$  is  $O_h$ . The invariance of  $H$  under  $O_h$  yields to molecular orbitals for  $\text{Ti}(\text{H}_2\text{O})_6^{3+}$  with well-defined properties with respect to the elements of  $O_h$ .

**Example 3.** A symmetry or invariance group of a Hamiltonian often appears as a direct product of groups. For instance, if we want to take into consideration both permutation and rotation symmetries in a complex atom with  $N$  electrons, we must combine  $S_N$  and  $O(3)$  into the direct product  $S_N \otimes O(3)$ . Furthermore, if we make the approximation that the electronic correlation is *negligible*, we can consider that  $S_N \otimes O(3)^{\otimes N}$  is an *approximate* invariance group. Then, we foresee that the chain  $S_N \otimes O(3)^{\otimes N} \supset S_N \otimes O(3)$  plays an important rôle for a  $N$ -electron atom.

**Example 4.** In the case of the simplest atom, i.e., the hydrogen atom, the group  $O(3)$  is not sufficient for a complete characterization of the wavefunctions. For the discrete spectrum, there exists a larger group, namely  $SO(4)$ , whose generators commute with the Hamiltonian  $H$  of the hydrogen atom. This group is an invariance group (its generators commute with  $H$  as a whole rather than with the kinetic and potential parts of  $H$  separately). Thus, the relevant chain of groups to be considered for the discrete spectrum is  $O(4) \supset O(3)$ . Such a chain makes it possible to completely characterize or classify the discrete eigenvectors of  $H$  and to explain their degeneracy.

**2. As classification groups.** On the other hand, we can use a single group or a chain of groups for labelling the eigenvectors of a Hamiltonian  $H$ . Here, the single group or some groups of the chain do not correspond to symmetries of  $H$ . The interest of such groups is to be found in the fact that they allow to classify or label state vectors (or wavefunctions) and interactions.

**Example 5.** Let us consider an ion with an electronic configuration  $nf^3$ ,  $nf = 4f$  (lanthanide ion) or  $5f$  (actinide ion). (The ion has several closed shells plus an  $nf$  shell that is partly-filled with 3 electrons.) The corresponding Hamiltonian involving kinetic and Coulomb interactions is invariant under  $O(3)$ . This invariance allows one to partially classify the  $C_{2(2\ell+1)}^N = 14!/(3!11!) = 364$  wavefunctions for the configuration  $nf^3$  ( $\ell = 3$  and  $N = 3$ ) with the angular momentum quantum numbers  $L$  and  $M_L$ . We can also use the spin quantum numbers  $S$  and  $M_S$  for labelling the wavefunctions. Thus, the spectral group  $SU(2)$  that labels the spin may be introduced in addition to the geometrical symmetry group  $O(3)$ . However, the group  $SU(2) \otimes O(3)$  is not sufficient for labelling completely the 364 state vectors  $|nf^3 \tau S M_S L M_L\rangle$  of the configuration

$nf^3$ . An additional label  $\tau$  is needed when two terms  $^{2S+1}L$  with the same  $S$  and the same  $L$  are permitted. For instance, there are two terms  $^2H$  ( $S = 1/2$  and  $L = 5$ ) in  $nf^3$  and we need two labels  $\tau_1$  and  $\tau_2$  for distinguishing them. It was shown by Racah [7] that this state labelling problem can be solved through the introduction of the chain of classification groups  $U(7) \supset SO(7) \supset G_2$ , where  $G_2$  is one of the five exceptional groups of Cartan. The group  $U(7)$  corresponds to the fact that any unitary transformation on the  $2\ell + 1 = 7$  orbitals for the shell  $nf$  does not change the physics of the problem. The restriction  $U(7) \rightarrow SO(7)$  indicates that we can consider real orbitals. Finally, the occurrence of  $G_2$  between  $SO(7)$  and  $SO(3)$  is a mathematical fact. As a result, the label  $\tau$  can be replaced by  $(w_1w_2w_3)(u_1u_2)$ , where the triplet  $(w_1w_2w_3)$  stands for an irreducible representation of the group  $SO(7)$  (of rank 3) and the doublet  $(u_1u_2)$  for an irreducible representation of the group  $G_2$  (of rank 2). Furthermore, the labelling afforded by the group  $U(7)$  is equivalent to the one given by  $S$  and  $M_S$ , so that it is not anymore necessary to consider the spectral group  $SU(2)$  for the spin quantum numbers. The chain  $U(7) \supset SO(7) \supset G_2 \supset SO(3)$  is thus appropriate for a  $nf^3$  ion. The group  $SO(3)$ , or  $O(3)$  if we want to describe the parity of the wavefunctions, is an invariance group (and a classification group too) and the remaining groups of the chain are classification groups only. This chain is sufficient for characterizing completely the 17 spectral terms  $^{2S+1}L$  of the configuration  $nf^3$  and their associated state vectors  $|nf^3(w_1w_2w_3)(u_1u_2)SM_SLM_L\rangle$ . For example, the two terms  $^2H$  correspond to  $\tau_1 = (210)(11)$  and  $\tau_2 = (210)(21)$ . We close by mentioning that the chain  $U(7) \supset SO(7) \supset G_2 \supset SO(3)$  is also extremely useful for classifying interactions like the Coulomb interactions between the three equivalent electrons of  $nf^3$ . The classification of both state vectors and interactions by means of irreducible representations of the groups of a chain is essential for an easy and systematic calculation of matrix elements.

**Example 6.** We continue with the ion of Example 5. We now take into account the spin-orbit interaction and we introduce the ion in a molecular or crystal environment with  $D_3$  (trigonal) symmetry. Then, it is interesting to replace the preceding state vectors by state vectors of the type  $|nf^3(w_1w_2w_3)(u_1u_2)SLJa\Gamma\gamma\rangle$ . This amounts to complement the chain of Example 5 by the chain  $SU(2) \supset D_3^*$ , where  $SU(2)$  describes the total angular momentum  $J$  and the spinor group  $D_3^*$  of  $D_3$  labels the levels of the ion in its environment. The label  $a$  is to be used when the irreducible representation  $(J)$  of  $SU(2)$  contains several times the irreducible representation  $\Gamma$  of  $D_3^*$  and the label  $\gamma$  distinguishes the various vectors transforming as  $\Gamma$ . It is interesting to note that the actual symmetry group is  $D_3$  and that all the other groups are classification groups only. Note

also that the labels  $a$  and  $\gamma$  are multiplicity labels without group-theoretical meaning.

**Example 7.** The problem of classifying state vectors can be seen as a problem of finding a complete set of commuting operators. This may be understood with the example of the Wigner-Hund  $SU(4)$  model of nuclei. The latter model combines the group  $SU(2)_T$ , which describes the Heisenberg isospin symmetry, with the group  $SU(2)_S$ , for the spin of the nucleons. The resulting group  $SU(2)_T \otimes SU(2)_S$  can be embedded in  $SU(4)$ . The  $SU(4)$  symmetry is an approximate symmetry for the nucleon-nucleon forces (it is broken by the Coulomb interaction between protons and the spin-orbit interaction for the nucleons). The convenient chain is then  $SU(4) \supset SU(2)_T \otimes SU(2)_S$  and the corresponding state vectors read  $|(p, q, r)\tau TM_T SM_S\rangle$ , where  $TM_T$  and  $SM_S$  refer to the group  $SU(2)_T$  and  $SU(2)_S$ , respectively, and  $(p, q, r)$  stands for an irreducible representation of  $SU(4)$ . The labels  $p, q, r, T, M_T, S$ , and  $M_S$  are not sufficient in general for a complete labelling of the state vectors. A further label  $\tau$  is necessary. It is difficult to find a group-theoretical significance of this ‘missing’ label. However, it can be completely characterized by the eigenvalues  $\omega$  and  $\varphi$  of two independent operators which commute with the three Casimir operators of  $SU(4)$ , the two isospin operators  $T^2$  and  $T_3$ , and the two spin operators  $S^2$  and  $S_3$ . This leads to state vectors of the form  $|(p, q, r)\omega\varphi TM_T SM_S\rangle$  which are common eigenvectors of nine commuting operators.

We now examine in a more quantitative way how to exploit the introduction of groups and chains of groups by establishing two links between group theory and quantum mechanics.

### 3 Connecting Group Theory and Quantum Mechanics

#### 3.1 The Wigner theorem

Let us consider a Hamiltonian  $H$ , defined on some Hilbert space  $\mathcal{E}$ , invariant under a finite or compact group  $G$ . We represent each element  $R$  of  $G$  by a linear operator  $U_R$  that acts on  $\mathcal{E}$ . The invariance of  $H$  under  $G$  means that

$$\forall R \in G \quad U_R^{-1} H U_R = H$$

(In other words,  $H$  commutes with the group, isomorphic to  $G$ , spanned by the set  $\{U_R : R \in G\}$ .) Let  $E_\lambda$  be an eigenvalue of  $H$  of degeneracy  $d$ . It thus exists  $d$  vectors  $\phi_{\lambda j}$  in  $\mathcal{E}$  such that

$$H\phi_{\lambda j} = E_\lambda\phi_{\lambda j} \quad j = 1, 2, \dots, d$$

We then have the series of trivial calculations

$$H(U_R\phi_{\lambda j}) = (HU_R)\phi_{\lambda j} = (U_RH)\phi_{\lambda j} = U_R(H\phi_{\lambda j}) = U_R(E_\lambda\phi_{\lambda j}) = E_\lambda(U_R\phi_{\lambda j})$$

As a result, the vector  $U_R\phi_{\lambda j}$  is an eigenvector of  $H$  with the eigenvalue  $E_\lambda$ . Therefore, we can write  $U_R\phi_{\lambda j}$  as a linear combination of the vectors  $\phi_{\lambda k}$  with  $k = 1, 2, \dots, d$ . Let us put

$$U_R\phi_{\lambda j} = \sum_{k=1}^d \phi_{\lambda k} D(R)_{kj}$$

where the coefficients of the linear combination, which depend on  $R$  as well as on  $k$  and  $j$ , are denoted as  $D(R)_{kj}$ . The coefficients  $D(R)_{kj}$  (for  $k$  and  $j = 1, 2, \dots, d$ ) define a matrix  $D(R)$ . It is straightforward to verify that

$$\forall R \in G \quad \forall S \in G \quad D(R)D(S) = D(RS)$$

so that  $D = \{D(R) : R \in G\}$  constitutes a  $d$ -dimensional representation of  $G$ . This result may be summarized by the following theorem [1].

**Theorem 1** (Wigner's theorem). The eigenvectors corresponding to a given eigenvalue of a Hermitean<sup>3</sup> operator  $H$  invariant under a finite or compact group  $G$  form a basis for a linear representation  $D$  of  $G$ .

Since the group  $G$  is finite or compact, there are two possibilities for  $D$ : The representation  $D$  is either *irreducible* or *completely reducible*. We then have two definitions.

**Definition 1.** If the representation  $D$  is irreducible, the degeneracy of the  $d$  functions  $\phi_{\lambda 1}, \phi_{\lambda 2}, \dots, \phi_{\lambda d}$  is said to be 'essential' or 'natural' or 'normal' with respect to the group  $G$ .

**Definition 2.** If the representation  $D$  is (completely) reducible, the  $d$  functions  $\phi_{\lambda 1}, \phi_{\lambda 2}, \dots, \phi_{\lambda d}$  are said to present an 'accidental' degeneracy with respect to the group  $G$ .

The Wigner theorem offers the possibility to classify wavefunctions and energy levels of a Hamiltonian invariant under a group  $G$  in terms of the irreducible representations of  $G$ . These irreducible representations constitute good quantum numbers for  $H$ . They are conserved in a sense to be explained in Section 4.7. Before giving examples, we conclude that a *symmetry* or *invariance* group is also a *classification* group (the converse may not be true).

---

<sup>3</sup>The Hermitean operator  $H$  may be replaced by a normal operator.



**Example 8.** Let

$$H = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \omega^2 x^2 \quad \omega > 0$$

be the Hamiltonian for a one-dimensional harmonic oscillator. Obviously, the operator  $H$  is invariant under the finite group  $S_2$  ( $S_2 \sim Z_2 \sim C_2$ ). This group possesses two elements  $E$  and  $I$  corresponding to  $E : x \mapsto x$  and  $I : x \mapsto -x$ . Thus, it has two irreducible representations  $g$  (gerade) and  $u$  (ungerade) that can be written  $g = (1, 1)$  and  $u = (1, -1)$  in the class space  $(E, I)$ . (Other notations employed in spectroscopy for  $g$  and  $u$  are  $[2]$  or  $\Gamma_1$  or  $A$  and  $[1, 1]$  or  $\Gamma_2$  or  $B$ , respectively.) It is well-known that the spectrum of  $H$  (energy levels  $E_n$  and wavefunctions  $\phi_n$ ) is given by

$$E_n = (n + \frac{1}{2})\omega \quad \phi_n(x) \sim H_n(\sqrt{\omega}x) \exp(-\frac{1}{2}\omega x^2) \quad \text{with} \quad n \in \mathbf{N}$$

( $H_n$  is the Hermite polynomial of degree  $n$ .) Here,  $d = 1$  for each level  $E_n$ . Consequently, there is no degeneracy and each wavefunction  $\phi_n$  must span a one-dimensional representation of the group  $S_2$ . This is indeed the case because the wavefunctions  $\phi_n$  are symmetric or antisymmetric. The spectrum of  $H$  is labelled by the irreducible representations of  $S_2$  :  $\phi_n$  with  $n$  even spans the representation  $g$  and  $\phi_n$  with  $n$  odd the representation  $u$ .

**Example 9.** The Hamiltonian  $H$  for a nonrelativistic hydrogenlike atom reads

$$H = -\frac{1}{2}\Delta - Z\frac{1}{r} \quad Z > 0 \quad (0)$$

(The hydrogen atom corresponds to  $Z = 1$ .) The discrete energy spectrum is given by

$$E_n = \frac{1}{n^2} E_1 \quad E_1 = -\frac{1}{2} Z^2 \quad n \in \mathbf{N}^*$$

The degeneracy degree for the level  $E_n$  is  $n^2 = \sum_{\ell=0}^{n-1} (2\ell + 1)$ . It corresponds to the  $n^2$  wavefunctions  $\phi_{n\ell m}$  with  $m = -\ell, -\ell + 1, \dots, \ell$  and  $\ell = 0, 1, \dots, n - 1$  associated to  $E_n$ . The kinetic energy  $T = -(1/2)\Delta$  and the potential energy  $V = -Z/r$  are separately invariant under the proper rotation group  $R(3)$  in three dimensions (isomorphic to  $SO(3)$ ). Therefore,  $H$  is invariant under  $SO(3)$  too (and even under  $O(3)$ ). The group  $SO(3)$  has a countable infinite number of irreducible representations  $(\ell)$  with  $\ell \in \mathbf{N}$ . The irreducible representation  $(\ell)$  is of dimension  $2\ell + 1$ . The representation  $D$ , arising from Wigner's theorem, associated to  $E_n$  is

$$D \equiv D_{E_n} = \bigoplus_{\ell=0}^{n-1} (\ell)$$

which is reducible for  $n \neq 1$ . As a consequence, the group  $\text{SO}(3)$  does not explain completely the degeneracy for  $E_n$  when  $n \neq 1$ . The discrete spectrum of  $H$  exhibits accidental degeneracies with respect to the *geometrical symmetry group*  $\text{SO}(3)$  except for  $n = 1$ . For  $n$  and  $\ell$  fixed, the group  $\text{SO}(3)$  explains the degeneracy of the  $2\ell + 1$  eigenvectors  $\{\phi_{n\ell m} : m = -\ell, -\ell + 1, \dots, \ell\}$ . However, it does not explain the degeneracy of eigenvectors corresponding to a given value of  $n$  and having different values of  $\ell$ . It is possible (see the appendix) to show that  $D_{E_n}$  turns out to be equivalent to the irreducible representation  $(j, j)$ , with  $j = (n - 1)/2$ , of the group  $\text{SO}(4) \sim \text{SU}(2) \otimes \text{SU}(2)/Z_2$ . (The irreducible representations of  $\text{SU}(2) \otimes \text{SU}(2)$  are denoted as  $(j_1, j_2)$  with  $2j_i \in \mathbf{N}$  for  $i = 1, 2$ .) The group  $\text{SO}(4)$  is called a *degeneracy group*. For  $n$  fixed, the degeneracy of the  $n^2$  eigenvectors  $\phi_{n\ell m}$  is natural with respect to  $\text{SO}(4)$ . This group completely explains the degeneracies for the discrete spectrum of  $H$  in the sense that each discrete level is associated to an irreducible representation of  $\text{SO}(4)$ . As a conclusion, the chain of groups  $\text{SO}(4) \supset \text{SO}(3)$  for the discrete spectrum contains two types of groups : the symmetry group  $\text{SO}(3)$  which describes the geometrical symmetries of  $T$  and  $V$  (and thus  $H$ ) and the degeneracy group  $\text{SO}(4)$  which labels the eigenvalues of  $H$ . The classification group  $\text{SO}(4)$  is also a symmetry group or invariance group for  $H$  in view of the fact that its generators commute with  $H$ . It describes the symmetries of  $T + V$  as a whole.

Besides the compact group  $\text{SO}(4)$  for the discrete spectrum, noncompact groups may be introduced for the rest of the spectrum. As a matter of fact, the pseudo-orthogonal group  $\text{SO}(3,1)$  describes the continuous spectrum and the Euclidean group  $E(3)$  the zero-energy point of the spectrum (see the appendix). These two groups play the rôle of classification groups and invariance groups.

The preceding results can be generalized for a hydrogenlike atom in  $N$  dimensions. The groups  $\text{SO}(N + 1)$ ,  $\text{SO}(N, 1)$  and  $E(N)$  can be seen to be invariance groups for the discrete, continuous and zero-energy spectra of the  $N$ -dimensional Coulomb system, respectively. These three groups have to be distinguished from the *noninvariance group*  $\text{SO}(N + 1, 2)$ . The latter noncompact group is not an invariance group in the sense that not all of its generators commute with the Hamiltonian of the  $N$ -dimensional hydrogen atom. It is rather a *dynamical group* in the sense that one of its irreducible representations contains all the wavefunctions for the spectrum of the Coulomb system in  $N$  dimensions and that some of its generators may connect subspaces associated to different eigenvalues of the spectrum. The ordinary case  $N = 3$ , which corresponds to  $\text{SO}(4, 2) \sim \text{SU}(2, 2)/Z_2$ , is studied at length in the literature.

**Example 10.** The Hamiltonian  $H$  for an isotropic harmonic oscillator in

$N = 3$  dimensions is

$$H = -\frac{1}{2}\Delta + \frac{1}{2}\omega^2 r^2 \quad \omega > 0$$

The spectrum of  $H$  is entirely discrete. The energy levels are

$$E_n = (n + \frac{3}{2})\omega \quad n \in \mathbf{N}$$

The subspace  $\mathcal{E}_n = \{\Psi_{n_1 n_2 n_3} : n_i \in \mathbf{N}, i = 1, 2, 3 \mid n_1 + n_2 + n_3 = n\}$ , where the  $\Psi$ 's are simple products of the  $\phi$ 's of Example 8, is associated to the level  $E_n$ . Thus, the degeneracy degree for the level  $E_n$  is  $C_{n+N-1}^n = (n+1)(n+2)/2$ . The kinetic energy  $T = -(1/2)\Delta$  and the potential energy  $V = (1/2)\omega^2 r^2$  are invariant under  $\text{SO}(3)$ . Therefore, the group  $\text{SO}(3)$  is a *geometrical symmetry group* for  $H$ . According to Wigner's theorem, the eigenfunctions in  $\mathcal{E}_n$  span a representation  $D \equiv D_{E_n}$ . This representation is in general reducible. (Hint : For  $n = 2$ , we have  $\dim \mathcal{E}_n = 6$  and it does not exist a true irreducible representation  $(\ell)$  of  $\text{SO}(3)$  such that  $2\ell + 1 = 6$ .) It is possible to show that the Hamiltonian  $H$ , as considered as a whole (by writing it in terms of annihilation and creation boson operators), is invariant under the group  $\text{SU}(3)$ . It turns out that the wavefunctions of  $\mathcal{E}_n$  generate the irreducible representation  $(n, 0)$  of  $\text{SU}(3)$ . The group  $\text{SU}(3)$  is thus a *degeneracy group*. (The irreducible representations of  $\text{SU}(3)$  are characterized by couples  $(p, q) \in \mathbf{N}^2$ . The dimension of the representation  $(p, q)$  is  $\dim(p, q) = (p+1)(q+1)(p+q+2)/2$ .) For instance, we have the associations

$$\begin{aligned} D_{E_1} &= (0, 0) = (0) : 1s \text{ shell } (\dim \mathcal{E}_1 = 1) \\ D_{E_2} &= (1, 0) = (1) : 1p \text{ shell } (\dim \mathcal{E}_2 = 3) \\ D_{E_3} &= (2, 0) = (0) \oplus (2) : 2s1d \text{ shell } (\dim \mathcal{E}_3 = 6) \\ D_{E_4} &= (3, 0) = (1) \oplus (3) : 2p1f \text{ shell } (\dim \mathcal{E}_4 = 10) \end{aligned}$$

where we have indicated the decompositions of the representations  $(n, 0)$  of  $\text{SU}(3)$  into representations  $(\ell)$  of  $\text{SO}(3)$  as well as the corresponding nuclear shells (cf., the Mayer-Jensen shell model and the Elliott  $\text{SU}(3)$  rotation model). We note that the levels  $E_1$  and  $E_2$  do not exhibit accidental degeneracy with respect to  $\text{SO}(3)$  but that  $E_3$  and  $E_4$  do. The first nuclear magic numbers  $A = 2, 8$ , and  $20$  correspond to the groupings  $1s$ ,  $1s + 1p$ , and  $1s + 1p + 2s1d$ , respectively.

The extension from the three-dimensional oscillator to the  $N$ -dimensional isotropic harmonic oscillator is immediate. In the  $N$ -dimensional case, the geometrical symmetry group is  $\text{SO}(N)$  and the group  $\text{SU}(N)$  is a degeneracy (and thus invariance) group. The corresponding spectrum has accidental degeneracy

with respect to  $\text{SO}(\mathbf{N})$ . However, all the degeneracies are natural with respect to  $\text{SU}(\mathbf{N})$ . It is to be noticed that the real noncompact symplectic group  $\text{Sp}(2N, \mathbf{R})$  is a useful noninvariance group. The chain  $\text{Sp}(2N, \mathbf{R}) \supset \text{SU}(N) \supset \text{SO}(N)$  is of importance when looking for a dynamical group for the  $N$ -dimensional oscillator system.

**Example 11.** We close this series with the example of a three-dimensional nonrelativistic Hamiltonian  $H = -(1/2)\Delta + V$  where  $V$  is a central potential with  $V(r) \neq -Z/r$  and  $V(r) \neq (1/2)\omega^2 r^2$ . The operators  $V$  and  $-(1/2)\Delta$  (and thus  $H$ ) are invariant under  $\text{SO}(3) \otimes C_i$ , where  $C_i \sim S_2$ . We know that the discrete spectrum, if any, corresponds in general to energies of type  $E_{n\ell}$ . The level  $E_{n\ell}$  is associated to  $\mathcal{E}_{n\ell} = \{R_{n\ell}(r)Y_{\ell m}(\theta, \varphi) : m = -\ell, -\ell + 1, \dots, \ell\}$ , a subspace of  $2\ell + 1$  wavefunctions. Here,  $\ell$  belongs to  $\mathbf{N}$  and  $n - \ell - 1$  is the number of nodes (excluding 0 and  $\infty$ ) of the radial wavefunction  $R_{n\ell}$ . The Wigner theorem can be invoked for both  $\text{SO}(3)$  and  $C_i$ . Let  $D \equiv D_{E_{n\ell}}$  be the representation (of  $\text{SO}(3)$  and  $C_i$ ) spanned by the subspace  $\mathcal{E}_{n\ell}$ . For the group  $\text{SO}(3)$ , we have  $D_{E_{n\ell}} \equiv (\ell)$ : The degeneracy for the energy level  $E_{n\ell}$  is natural with respect to the group  $\text{SO}(3)$ . On the other hand, the behaviour under the group  $C_i$  of the vectors of  $\mathcal{E}_{n\ell}$  is trivial. The group  $C_i$  consists of the elements  $E : \vec{r} \mapsto \vec{r}$  and  $I : \vec{r} \mapsto -\vec{r}$ . Then, for  $I$  (which corresponds to  $\theta \mapsto \pi - \theta$  and  $\varphi \mapsto \varphi + \pi$ ), we have

$$U_I : R_{n\ell}(r)Y_{\ell m}(\theta, \varphi) \mapsto (-1)^\ell R_{n\ell}(r)Y_{\ell m}(\theta, \varphi)$$

Therefore, the subspace  $\mathcal{E}_{n\ell}$  constitutes a basis for a reducible representation of  $C_i$ : The degeneracy of the  $2\ell + 1$  wavefunctions of  $E_{n\ell}$  is accidental with respect to the group  $C_i$ . The wavefunctions  $R_{n\ell}Y_{\ell m}$  may be labelled by irreducible representations of  $C_i$  since they are even or odd under  $C_i$  according to as  $\ell$  is even or odd. Therefore, the decomposition of  $D_{E_{n\ell}}$  leads to  $D_{E_{n\ell}} = (2\ell + 1)g$  for  $\ell$  even or  $D_{E_{n\ell}} = (2\ell + 1)u$  for  $\ell$  odd.

### 3.2 The restriction group $\rightarrow$ subgroup

The concept of a chain of groups  $G_0 \supset G_1$  is important in physics especially in connection with symmetry breaking mechanisms and/or perturbation theory. In the framework of perturbation theory, the group  $G_0$  may be an invariance group for an unperturbed Hamiltonian  $H_0$  while the subgroup  $G_1$  of  $G_0$  may be an invariance group for a perturbed Hamiltonian  $H_0 + H_1$ . The passage from  $H_0$  to  $H_0 + H_1$  thus corresponds to a symmetry breaking where the symmetry of the Hamiltonian is lowered from  $G_0$  to  $G_1$ . A basic result concerning the restriction  $G_0 \rightarrow G_1$  is given by the following theorem.

**Theorem 2.** Let  $D_0 = \{D_0(R) : R \in G_0\}$  be a linear representation, of dimension  $d$ , of a group  $G_0$ . The restriction

$$D_1 = \{D_1(R) = D_0(R) : R \in G_1 \subset G_0\}$$

of  $D_0$  to a subgroup  $G_1$  of the group  $G_0$  furnishes a representation of  $G_1$ .

The proof easily follows from the fact that  $\forall R \in G_1$  and  $\forall S \in G_1$  we have  $D_1(R)D_1(S) = D_1(RS)$ . Therefore, every representation of  $G_0$  yields a representation of  $G_1$ . If  $D_0$  is a reducible representation of  $G_0$ , then  $D_1$  is necessarily a reducible representation of  $G_1$ . On the other hand, if  $D_0$  is an irreducible representation of  $G_0$ , then the representation  $D_1$  may be a reducible or irreducible representation of  $G_1$ .

Theorem 2 is very useful in the case of external symmetry breaking, i.e., in the case where the geometrical symmetry of a system is lowered through some external action as, for example, in the Zeeman effect and in the (homogeneous or inhomogeneous<sup>4</sup>) Stark effect. The restriction  $G_0 \rightarrow G_1$ , in terms of irreducible representations of  $G_0$  and  $G_1$ , is of central importance to see how the energy levels of  $H_0$  evolve when turning on the perturbation  $H_1$ . This level splitting when passing from the symmetry  $G_0$  to the lower symmetry  $G_1$  is formally obtained by looking at the decomposition of the irreducible representations of  $G_0$  into a direct sums of irreducible representations of  $G_1$ .

**Example 12.** Let us consider the case of a complex ion with configuration  $4f^1$ , like the ion  $\text{Ce}^{3+}$ , embedded in a crystal environment of octahedral (or cubical) symmetry. If we do not consider the spin-orbit interaction for the  $4f$  electron, the ground state for the configuration  $4f^1$  of the free ion is a term  $^2F$  ( $S = s = \frac{1}{2}$ ,  $L = \ell = 3$ ). This term spans the irreducible representation  $(3_u)$  (of dimension  $d = 7$ ) of the group  $O(3)$ , an invariance group for the free ion. (The irreducible representations of the direct product  $O(3) \sim SO(3) \otimes C_i$  are of type  $(\ell_g)$  or  $(\ell_u)$  with  $\ell \in \mathbf{N}$ .) By using standard methods, we can show that the decomposition of  $(3_u)$  into irreducible representations of the complete octahedral group  $O_h = O \otimes C_i$  leads to

$$(3_u) = A_{2u} \oplus T_{1u} \oplus T_{2u}$$

where  $T_{1u}$  and  $T_{2u}$  are two three-dimensional irreducible representations of  $O_h$  and  $A_{2u}$  is a one-dimensional representation of  $O_h$ . Therefore, the atomic term  $^2F$  gives rise to three (crystal-field or molecular) terms  $^2A_{2u}$ ,  $^2T_{1u}$  and  $^2T_{2u}$  when we pass from the free ion to the ion in its cubical surrounding.

---

<sup>4</sup>For instance, the inhomogeneous Stark effect arises when a partly-filled shell ion is embedded in a crystal ; such an ion is thus subjected to an (inhomogeneous) crystalline electric field which has, according to Curie's principle, the symmetry of the environment of the ion.

**Example 13.** To go further with Example 12, we can now deal with the case where we take into consideration the spin-orbit interaction for the  $4f$  electron. The term  ${}^2F$  then splits into two multiplets  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$ . The relevant group for the free ion is  $SU(2)$  (with  $SO(3) \sim SU(2)/Z_2$ ) and the one for the ion in its cubical surrounding is the ‘doubled’ or spinor group  $O^*$  (with  $O \sim O^*/Z_2$ ). The state vectors for the multiplets  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  span the irreducible representations  $(5/2)$  and  $(7/2)$  (of dimensions  $d = 6$  and  $d = 8$ ) of  $SU(2)$ , respectively. The restriction  $SU(2) \rightarrow O^*$  yields

$$(5/2) = \Gamma_7 \oplus \Gamma_8 \quad (7/2) = \Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8$$

so that the multiplets  ${}^2F_{7/2}$  and  ${}^2F_{5/2}$  are split (in the absence of accidental degeneracies) according to one doublet ( $\Gamma_7$ ) plus one quadruplet ( $\Gamma_8$ ) and two doublets ( $\Gamma_6$  and  $\Gamma_7$ ) plus one quadruplet ( $\Gamma_8$ ), respectively. (The irreducible representations of  $SU(2)$  are denoted as  $(j)$  with  $2j \in \mathbf{N}$  while  $\Gamma_6$ ,  $\Gamma_7$  and  $\Gamma_8$  are irreducible representations of  $O^*$ .)

## 4 Wigner - Racah Algebra

An important task in spectroscopy is to calculate matrix elements in order to determine energy spectra and transition intensities. One way to incorporate symmetry considerations connected to a chain of groups (involving symmetry groups and classification groups) is to use the ‘Wigner-Racah calculus’ associated to the chain under consideration. The ‘Wigner-Racah calculus’ or ‘Wigner-Racah algebra’ associated to a group  $G$  or a chain of groups  $G \supset H$  is generally understood as the set of algebraic manipulations concerning the coupling and recoupling coefficients for the group  $G$ . This ‘algebra’ may be also understood as a true algebra (in the mathematical sense) : It is the (infinite dimensional) Lie algebra spanned by the irreducible unit tensor operators or Wigner operators of the group  $G$ . We shall mainly focus here on the basic aspects of the ‘algebra’ of the coupling and recoupling coefficients of  $G$ . The Wigner-Racah calculus was originally developed for simply-reducible (i.e., ambivalent<sup>5</sup> plus multiplicity-free<sup>6</sup>) groups [4, 5, 6], for the rotation group [5, 7] and for some groups of interest in molecular and condensed matter physics [8, 9, 10]. The extension to an arbitrary finite or compact group can be achieved and we present in what follows the ingredients for such an extension (that is of great interest in nuclear, atomic, molecular, and condensed matter physics as well as in quantum chemistry).

---

<sup>5</sup>A group  $G$  is said to be ambivalent if each element of  $G$  and its inverse belong to a same conjugation class.

<sup>6</sup>A group  $G$  is said to be multiplicity-free if the Kronecker product of two arbitrary irreducible representations of  $G$  contains at most once each irreducible representation of  $G$ .

## 4.1 Preliminaries

Let us consider an arbitrary finite or compact continuous group  $G$  having the irreducible representation classes (IRC's)  $a, b, \dots$ . The identity IRC, customarily noted  $A_1$  or  $\Gamma_1$  in molecular physics, is denoted by 0. To each IRC  $a$ , we associate a unitary matrix representation  $\mathcal{D}^a$ . Let  $[a]$  be the dimension of  $\mathcal{D}^a$ . The  $\alpha$ - $\alpha'$  matrix element of the representative  $\mathcal{D}^a(R)$  for the element  $R$  in  $G$  is written  $\mathcal{D}^a(R)_{\alpha\alpha'}$ . (For  $a = 0$ , we use  $\alpha = \alpha' = 0$ .) The sum  $\chi^a(R) = \sum_{\alpha} \mathcal{D}^a(R)_{\alpha\alpha}$  stands for the character of  $R$  in  $\mathcal{D}^a$ . The  $\mathcal{D}^a(R)_{\alpha\alpha'}$  and  $\chi^a(R)$  satisfy orthogonality relations (e.g., the so-called great orthogonality theorem) that are very familiar to the physicist. Finally, note that  $\int_G \dots dR$  identifies to  $\sum_{R \in G} \dots$  and that  $|G| = \int_G dR$  corresponds to the order of  $G$  in the case where  $G$  is a finite group or the volume of  $G$  in the case where  $G$  is a continuous compact group.

## 4.2 Clebsch-Gordan coefficients

The direct product  $a \otimes b$  of two IRC's  $a$  and  $b$  of  $G$  can be in general decomposed into a direct sum of IRC's of  $G$ . This leads to the Clebsch-Gordan series

$$a \otimes b = \bigoplus_c \sigma(c|a \otimes b) c \quad (1)$$

where  $\sigma(c|a \otimes b)$  denotes the number of times the IRC  $c$  occurs in  $a \otimes b$ . The integers  $\sigma(c|a \otimes b)$  may be determined through the character formula

$$\sigma(c|a \otimes b) = |G|^{-1} \int_G \chi^c(R)^* \chi^a(R) \chi^b(R) dR \quad (2)$$

In terms of matrix representations, Eq. (1) reads

$$\mathcal{D}^a \otimes \mathcal{D}^b \simeq \bigoplus_c \sigma(c|a \otimes b) \mathcal{D}^c \quad (3)$$

Therefore, there exists a unitary matrix  $U^{ab}$  such that

$$(U^{ab})^\dagger \mathcal{D}^a(R) \otimes \mathcal{D}^b(R) U^{ab} = \bigoplus_c \sigma(c|a \otimes b) \mathcal{D}^c(R) \quad (4)$$

$$\mathcal{D}^a(R) \otimes \mathcal{D}^b(R) = \bigoplus_c \sigma(c|a \otimes b) U^{ab} \mathcal{D}^c(R) (U^{ab})^\dagger \quad (5)$$

for any  $R$  in  $G$ . It is a simple exercise in linear algebra to transcribe (4) and (5) in matrix elements. We thus have

$$\begin{aligned} \sum_{\alpha\beta\alpha'\beta'} (ab\alpha\beta|\rho c\gamma)^* \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} (ab\alpha'\beta'|\rho'c'\gamma') \\ = \Delta(c|a \otimes b) \delta(\rho'\rho) \delta(c'c) \mathcal{D}^c(R)_{\gamma\gamma'} \end{aligned} \quad (6)$$

and

$$\mathcal{D}^a(R)_{\alpha\alpha'}\mathcal{D}^b(R)_{\beta\beta'} = \sum_{\rho c\gamma\gamma'} (ab\alpha\beta|\rho c\gamma)\mathcal{D}^c(R)_{\gamma\gamma'}(ab\alpha'\beta'|\rho c\gamma')^* \quad (7)$$

for any  $R$  in  $G$ . In Eqs. (6) and (7),  $(ab\alpha\beta|\rho c\gamma)$  stands for an element of the matrix  $U^{ab}$  :

$$(ab\alpha\beta|\rho c\gamma) = (U^{ab})_{\alpha\beta,\rho c\gamma} \quad (8)$$

Each row index of  $U^{ab}$  consists of two labels ( $\alpha$  and  $\beta$ ) according to the rules of the direct product of two matrices. This is the same thing for each column index of  $U^{ab}$ , i.e., two labels ( $c$  and  $\gamma$ ) are required. However, when  $c$  appears several times in  $a \otimes b$ , a third label (the multiplicity label  $\rho$ ) is necessary besides  $c$  and  $\gamma$ . Hence, the summation over  $\rho$  in (7) ranges from 1 to  $\sigma(c|a \otimes b)$ . Finally, in Eq. (6),  $\delta$  denotes the usual Kronecker delta while  $\Delta(c|a \otimes b) = 0$  or 1 according to whether  $c$  is contained or not in  $a \otimes b$ .

The matrix elements  $(ab\alpha\beta|\rho c\gamma)$  are termed Clebsch-Gordan coefficients (CGc's) or vector coupling coefficients. The present introduction clearly emphasizes that the CGc's of a group  $G$  are nothing but the elements of the unitary matrix which reduces the direct product of two irreducible matrix representations of  $G$ . As a consequence, the CGc's satisfy two orthonormality relations associated to the unitary property of  $U^{ab}$  :

$$\sum_{\alpha\beta} (ab\alpha\beta|\rho c\gamma)^*(ab\alpha\beta|\rho'c'\gamma') = \Delta(c|a \otimes b)\delta(\rho'\rho)\delta(c'c)\delta(\gamma'\gamma) \quad (9)$$

$$\sum_{\rho c\gamma} (ab\alpha\beta|\rho c\gamma)(ab\alpha'\beta'|\rho c\gamma)^* = \delta(\alpha'\alpha)\delta(\beta'\beta) \quad (10)$$

Note that (9) and (10) are conveniently recovered by specializing  $R$  to the unit element  $E$  of  $G$  in (6) and (7), respectively.

Equations (6) and (7) show that the CGc's are basis-dependent coefficients. In this regard, it is important to realize that (6) and (7) are not sufficient to define unambiguously the CGc's of the group  $G$  once its irreducible representation matrices are known. As a matter of fact, the relation

$$(ab\alpha\beta|rc\gamma) = \sum_{\rho} (ab\alpha\beta|\rho c\gamma)M(ab, c)_{\rho r} \quad (11)$$

where  $M(ab, c)$  is an arbitrary unitary matrix, defines a new set of CGc's since (6) and (7) are satisfied by making replacements of the type  $\rho \rightarrow r$ . The CGc's associated to a definite choice for the irreducible representation matrices of  $G$  are thus defined up to a unitary transformation, a fact that may be exploited to generate special properties of the CGc's.



Various relations involving elements of irreducible representation matrices and CGc's can be derived from (6) and (7) by using the unitary property both for the representation matrices and the Clebsch-Gordan matrices. For instance, from (6) we obtain

$$\sum_{\alpha'\beta'} \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} (ab\alpha'\beta'|\rho c\gamma') = \sum_{\gamma} \mathcal{D}^c(R)_{\gamma\gamma'} (ab\alpha\beta|\rho c\gamma) \quad (12)$$

$$(ab\alpha'\beta'|\rho c\gamma') = \sum_{\alpha\beta\gamma} (ab\alpha\beta|\rho c\gamma) \mathcal{D}^a(R)_{\alpha\alpha'}^* \mathcal{D}^b(R)_{\beta\beta'}^* \mathcal{D}^c(R)_{\gamma\gamma'} \quad (13)$$

for any  $R$  in  $G$ . In the situation where the elements of the irreducible representation matrices of  $G$  are known, (12) or (13) provides us with a system of linear equations useful for the calculation of the CGc's of  $G$ .

The combination of (7) with the great orthogonality theorem for  $G$  yields the integral relation

$$|G|^{-1} \int_G \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} \mathcal{D}^c(R)_{\gamma\gamma'}^* dR = [c]^{-1} \sum_{\rho} (ab\alpha\beta|\rho c\gamma) (ab\alpha'\beta'|\rho c\gamma')^* \quad (14)$$

which also is useful for the calculation of the CGc's of  $G$  in terms of the elements of the irreducible representation matrices of  $G$ . Note that when  $a \otimes b$  is multiplicity-free (i.e., when there is no summation on  $\rho$  in (14)), Eq. (14) allows us to determine the  $(ab\alpha\beta|\rho c\gamma)$  for all  $\alpha, \beta$  and  $\gamma$  up to an arbitrary phase factor  $h(ab, c)$ ; more precisely, we then have

$$(ab\alpha\beta|\rho c\gamma) = e^{ih(ab,c)} \frac{\int_G \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} \mathcal{D}^c(R)_{\gamma\gamma'}^* dR}{\left\{ \frac{|G|}{[c]} \int_G \mathcal{D}^a(R)_{\alpha'\alpha'} \mathcal{D}^b(R)_{\beta'\beta'} \mathcal{D}^c(R)_{\gamma'\gamma'}^* dR \right\}^{\frac{1}{2}}} \quad (15)$$

It appears from Eqs. (12)-(15) that  $c$  does not generally play the same rôle as  $a$  and  $b$  in  $(ab\alpha\beta|\rho c\gamma)$ . Therefore,  $(ab\alpha\beta|\rho c\gamma)$  does not generally exhibit simple symmetry properties under permutation of  $a, b$  and  $c$ . It is to be showed in the following how the CGc's may be symmetrized thanks to a  $2-a\alpha$  symbol.

### 4.3 The $2-a\alpha$ symbol

Let us define the  $2-a\alpha$  symbol through

$$\begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} = [a]^{\frac{1}{2}} (ba\beta\alpha|00) \quad (16)$$

The  $2-a\alpha$  symbol makes it possible to pass from a given irreducible matrix representation to its complex conjugate. This is reflected by the two relations

$$\sum_{\alpha\alpha'} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^* \mathcal{D}^a(R)_{\alpha\alpha'} \begin{pmatrix} a & b' \\ \alpha' & \beta' \end{pmatrix} = \Delta(0|a \otimes b) \delta(b'b) \mathcal{D}^b(R)_{\beta\beta'}^* \quad (17)$$

$$\sum_{\beta\beta'} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} \mathcal{D}^b(R)_{\beta\beta'}^* \begin{pmatrix} a' & b \\ \alpha' & \beta' \end{pmatrix}^* = \Delta(0|a \otimes b) \delta(a'a) \mathcal{D}^a(R)_{\alpha\alpha'} \quad (18)$$

that hold for any  $R$  in  $G$ . The proof of (17) and (18) is delicate ; it starts with the introduction of (16) into the left-hand sides of (17) and (18) and requires the successive use of (13), (7), (9) and (13), of the great orthogonality theorem, and of (9). By taking  $R = E$  in (17) and (18), we get the useful relations

$$\sum_{\alpha} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^* \begin{pmatrix} a & b' \\ \alpha & \beta' \end{pmatrix} = \Delta(0|a \otimes b) \delta(b'b) \delta(\beta'\beta) \quad (19)$$

$$\sum_{\beta} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} \begin{pmatrix} a' & b \\ \alpha' & \beta \end{pmatrix}^* = \Delta(0|a \otimes b) \delta(a'a) \delta(\alpha'\alpha) \quad (20)$$

The  $2-a\alpha$  symbol turns out to be of relevance for handling phase problems. In this regard, both (17) and (18) lead to

$$\delta(a'a) \sum_{\alpha\alpha'} \begin{pmatrix} a & a' \\ \alpha & \alpha' \end{pmatrix}^* \begin{pmatrix} a' & a \\ \alpha' & \alpha \end{pmatrix} = \Delta(0|a \otimes a') [a] c_a \quad (21)$$

where the Frobenius-Schur coefficient

$$c_a = |G|^{-1} \int_G \chi^a(R^2) dR \quad (22)$$

is 1,  $-1$ , or 0 according to as  $\mathcal{D}^a$  is orthogonal, symplectic, or complex. The conjugating matrix to pass from  $\mathcal{D}^a$  to  $(\mathcal{D}^a)^*$  satisfies

$$c_a \begin{pmatrix} a' & a \\ \alpha' & \alpha \end{pmatrix} = \delta(a'a) \begin{pmatrix} a & a' \\ \alpha & \alpha' \end{pmatrix} \quad (23)$$

(cf., the Frobenius-Schur theorem).

#### 4.4 The $(3 - a\alpha)_\rho$ symbol

We now define the  $(3-a\alpha)_\rho$  symbol via

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho = \sum_{\rho'c'\gamma'} [c']^{-\frac{1}{2}} M(ba, c')_{\rho'\rho} \begin{pmatrix} c & c' \\ \gamma & \gamma' \end{pmatrix} (ba\beta\alpha|\rho'c'\gamma') \quad (24)$$

where  $M(ba, c')$  is an arbitrary unitary matrix. Conversely, each CGc can be developed in terms of  $(3-a\alpha)_\rho$  symbols since the inversion of (24) gives

$$(ab\alpha\beta|\rho c\gamma) = [c]^{\frac{1}{2}} \sum_{\rho'c'\gamma'} M(ab, c)_{\rho\rho'}^* \begin{pmatrix} c' & c \\ \gamma' & \gamma \end{pmatrix}^* \begin{pmatrix} b & a & c' \\ \beta & \alpha & \gamma' \end{pmatrix}_{\rho'} \quad (25)$$

All the relations involving CGc's may be transcribed in function of  $(3-a\alpha)_\rho$  symbols. For example, the introduction of (25) into (6) and (7) yields after nontrivial calculations

$$\begin{aligned} \sum_{\alpha\beta\alpha'\beta'} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho^* \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} \begin{pmatrix} a & b & c' \\ \alpha' & \beta' & \gamma' \end{pmatrix}_{\rho'} \\ = \Delta(0|a \otimes b \otimes c) \delta(\rho'\rho) \delta(c'c) [c]^{-1} \mathcal{D}^c(R)_{\gamma\gamma'}^* \end{aligned} \quad (26)$$

and

$$\mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} = \sum_{\rho c \gamma \gamma'} [c] \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho \mathcal{D}^c(R)_{\gamma\gamma'}^* \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}_\rho^* \quad (27)$$

for any  $R$  in  $G$ . The orthogonality relations

$$\sum_{\alpha\beta} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho^* \begin{pmatrix} a & b & c' \\ \alpha & \beta & \gamma' \end{pmatrix}_{\rho'} = \Delta(0|a \otimes b \otimes c) \delta(\rho'\rho) \delta(c'c) \delta(\gamma'\gamma) [c]^{-1} \quad (28)$$

$$\sum_{\rho c \gamma} [c] \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma \end{pmatrix}_\rho^* = \delta(\alpha'\alpha) \delta(\beta'\beta) \quad (29)$$

follow by putting  $R = E$  in (26) and (27).

Relation (26) and its dual relation (27) show that  $\mathcal{D}^a$ ,  $\mathcal{D}^b$  and  $\mathcal{D}^c$  present the same variance. Thus, the behaviour of the  $(3-a\alpha)_\rho$  symbol under permutation of  $a$ ,  $b$  and  $c$  should be easier to describe than the one of the CGc  $(ab\alpha\beta|\rho c\gamma)$ . This is reflected by the integral relation (to be compared to (14))

$$|G|^{-1} \int_G \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} \mathcal{D}^c(R)_{\gamma\gamma'} dR = \sum_\rho \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}_\rho^* \quad (30)$$

which may be proved directly by combining (27) with the great orthogonality theorem for the group  $G$ . When the triple direct product  $a \otimes b \otimes c$  contains the IRC 0 of  $G$  only once (i.e., when there is no label  $\rho$  and no summation in (30)), Eq. (30) shows that the square modulus of the  $3-a\alpha$  symbol is invariant under permutation of its columns. In this case, we may take advantage of the arbitrariness of the matrix  $M$  in (11) or (24) to produce convenient symmetry properties of the  $3-a\alpha$  symbol under permutation of its columns. By way of illustration, let us mention the following result : For  $G$  simply reducible, it is possible to arrange that the numerical value of the  $3-a\alpha$  symbol be multiplied by the phase factor  $(-1)^{a+b+c}$ , with  $(-1)^{2x} = c_x$ , under an odd permutation of its columns ; consequently, the numerical value of the  $3-a\alpha$  symbol remains unchanged under an even permutation of its columns (since  $c_a c_b c_c = 1$ ).

## 4.5 Recoupling coefficients

We now define two new coefficients

$$\begin{aligned} (a(bc)\rho_{bc}c_{bc}\rho'd'\delta'|(ab)\rho_{ab}c_{ab}c\rho d\delta) &= \sum_{\alpha\beta\gamma\gamma_{ab}\gamma_{bc}} (ab\alpha\beta|\rho_{ab}c_{ab}\gamma_{ab})(c_{ab}c\gamma_{ab}\gamma|\rho d\delta) \\ &\quad \times (bc\beta\gamma|\rho_{bc}c_{bc}\gamma_{bc})^*(ac_{bc}\alpha\gamma_{bc}|\rho'd'\delta')^* \end{aligned} \quad (31)$$

and

$$\begin{aligned} &((ac)\rho_{ac}c_{ac}(bd)\rho_{bd}c_{bd}\rho'e'\varepsilon'|(ab)\rho_{ab}c_{ab}(cd)\rho_{cd}c_{cd}\rho e\varepsilon) \\ &= \sum_{\alpha\beta\gamma\delta} \sum_{\gamma_{ab}\gamma_{cd}\gamma_{ac}\gamma_{bd}} (ab\alpha\beta|\rho_{ab}c_{ab}\gamma_{ab})(cd\gamma\delta|\rho_{cd}c_{cd}\gamma_{cd})(c_{ab}c_{cd}\gamma_{ab}\gamma_{cd}|\rho e\varepsilon) \\ &\quad \times (ac\alpha\gamma|\rho_{ac}c_{ac}\gamma_{ac})^*(bd\beta\delta|\rho_{bd}c_{bd}\gamma_{bd})^*(c_{ac}c_{bd}\gamma_{ac}\gamma_{bd}|\rho'e'\varepsilon')^* \end{aligned} \quad (32)$$

The introduction in these definitions of (13) and the use of the great orthogonality theorem for  $G$  leads to the properties

$$\begin{aligned} &(a(bc)\rho_{bc}c_{bc}\rho'd'\delta'|(ab)\rho_{ab}c_{ab}c\rho d\delta) \\ &= \delta(d'd)\delta(\delta'\delta)[d]^{-1} \sum_{\delta} (a(bc)\rho_{bc}c_{bc}\rho'd\delta|(ab)\rho_{ab}c_{ab}c\rho d\delta) \end{aligned} \quad (33)$$

and

$$\begin{aligned} &((ac)\rho_{ac}c_{ac}(bd)\rho_{bd}c_{bd}\rho'e'\varepsilon'|(ab)\rho_{ab}c_{ab}(cd)\rho_{cd}c_{cd}\rho e\varepsilon) \\ &= \delta(e'e)\delta(\varepsilon'\varepsilon)[e]^{-1} \sum_{\varepsilon} ((ac)\rho_{ac}c_{ac}(bd)\rho_{bd}c_{bd}\rho'e\varepsilon|(ab)\rho_{ab}c_{ab}(cd)\rho_{cd}c_{cd}\rho e\varepsilon) \end{aligned} \quad (34)$$

so that the recoupling coefficients defined by (31) and (32) are basis-independent (i.e., they do not depend on the labels of type  $\alpha$ ) in contradistinction to the coupling coefficients  $(ab\alpha\beta|\rho c\gamma)$ . In a way paralleling the passage from the coupling coefficients to the  $(3-a\alpha)_\rho$  symbol, one can define  $(6-a)_{4\rho}$  and  $(9-a)_{6\rho}$  symbols from the recoupling coefficients defined by (31)-(34). The defining expressions  $(6-a)_{4\rho}$  and  $(9-a)_{6\rho}$  symbols are very complicated and not especially instructive in the case of an arbitrary compact group  $G$ . Hence, they shall be omitted as well as the defining expressions for higher  $(3N-a)_{2N\rho}$  symbols corresponding to the recoupling of  $N > 3$  IRC's. Finally, note that the recoupling coefficients and their associated  $(3N-a)_{2N\rho}$  symbols,  $N > 1$ , for a group  $G$  can be connected to other basis-independent quantities, viz., the characters of  $G$ .

## 4.6 Irreducible tensorial sets

Let  $\{|\tau a\alpha\rangle : \alpha = 1, 2, \dots, [a]\}$  be a basis for the irreducible matrix representation  $\mathcal{D}^a$  of  $G$ . The vectors  $|\tau a\alpha\rangle$  are defined on a unitary or pre-Hilbert space

$\mathcal{E}$  (indeed, a Hilbert space in the quantum-mechanical applications) and there exists an application  $R \mapsto U_R$  such that

$$U_R|\tau a\alpha\rangle = \sum_{\alpha'=1}^{[a]} |\tau a\alpha'\rangle \mathcal{D}^a(R)_{\alpha'\alpha} \quad (35)$$

for any  $R$  in  $G$ . The set  $\{|\tau a\alpha\rangle : \alpha = 1, 2, \dots, [a]\}$  is referred to as an irreducible tensorial set (ITS) of vectors associated to  $\mathcal{D}^a$ . The label  $\tau$  may serve to distinguish the various ITS' of vectors associated to the same irreducible matrix representation  $\mathcal{D}^a$ . (In practical applications, this label consists of various quantum numbers arising from nuclear, or atomic or molecular configurations.) In this connection, note the following standardization : It is always possible to arrange that  $\{|\tau a\alpha\rangle : \alpha = 1, 2, \dots, [a]\}$  and  $\{|\tau' a\alpha\rangle : \alpha = 1, 2, \dots, [a]\}$  span the same matrix representation  $\mathcal{D}^a$  rather than two equivalent representations.

From two ITS'  $\{|\tau_a a\alpha\rangle : \alpha = 1, 2, \dots, [a]\}$  and  $\{|\tau_b b\beta\rangle : \beta = 1, 2, \dots, [b]\}$ , we can construct another ITS of vectors. Let us define

$$|\tau_a \tau_b ab\rho c\gamma\rangle = \sum_{\alpha\beta} |\tau_a a\alpha\rangle \otimes |\tau_b b\beta\rangle (ab\alpha\beta|\rho c\gamma) \quad (36)$$

Then, as a simple corollary of (7), the set  $\{|\tau_a \tau_b ab\rho c\gamma\rangle : \gamma = 1, 2, \dots, [c]\}$  can be shown to be an ITS associated to  $\mathcal{D}^c$ .

In a similar way, let us consider a set  $\{T_\alpha^a : \alpha = 1, 2, \dots, [a]\}$  of (linear) operators defined on  $\mathcal{E}$  and such that

$$U_R T_\alpha^a U_R^{-1} = \sum_{\alpha'=1}^{[a]} T_{\alpha'}^a \mathcal{D}^a(R)_{\alpha'\alpha} \quad (37)$$

for any  $R$  in  $G$ . This set is called an ITS of operators associated to  $\mathcal{D}^a$ . We also say that this set defines an irreducible tensor operator  $\mathbf{T}^a$  associated to  $\mathcal{D}^a$ . Note the implicit standardization : The sets  $\{T_\alpha^a : \alpha = 1, 2, \dots, [a]\}$  and  $\{U_\alpha^a : \alpha = 1, 2, \dots, [a]\}$  span the same matrix representation  $\mathcal{D}^a$  rather than two equivalent representations.

In full analogy with (36), we define

$$\{T^a \otimes U^b\}_\gamma^{\rho c} = \sum_{\alpha\beta} T_\alpha^a U_\beta^b (ab\alpha\beta|\rho c\gamma) \quad (38)$$

from the two ITS'  $\{T_\alpha^a : \alpha = 1, 2, \dots, [a]\}$  and  $\{U_\alpha^b : \beta = 1, 2, \dots, [b]\}$ . As a result, the set  $\{\{T^a \otimes U^b\}_\gamma^{\rho c} : \gamma = 1, 2, \dots, [c]\}$  is an ITS of operators associated to  $\mathcal{D}^c$ . We say that  $\{\mathbf{T}^a \otimes \mathbf{U}^b\}$  is the direct product of the irreducible tensor

operators  $\mathbf{T}^a$  and  $\mathbf{U}^b$ . Observe that this direct product defines a tensor operator which is reducible in general. Equation (38) gives the various irreducible components of  $\{\mathbf{T}^a \otimes \mathbf{U}^b\}$ .

#### 4.7 The Wigner-Eckart theorem

The connection between most of the quantities introduced up to now appears in the calculation of the matrix element  $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha)$ , the scalar product on  $\mathcal{E}$  of the vector  $T_\beta^b|\tau a\alpha)$  by the vector  $|\tau'a'\alpha')$ . By developing the identity

$$(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) = (\tau'a'\alpha'|U_R^\dagger U_R T_\beta^b U_R^{-1} U_R|\tau a\alpha) \quad (39)$$

we get after some manipulations the basic theorem.

**Theorem 3** (Wigner-Eckart's theorem). The scalar product  $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha)$  can be decomposed as

$$(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) = \sum_\rho (\tau'a' || T^b || \tau a)_\rho \sum_{a''\alpha''} \begin{pmatrix} a'' & a' \\ \alpha'' & \alpha' \end{pmatrix} \begin{pmatrix} b & a & a'' \\ \beta & \alpha & \alpha'' \end{pmatrix}_\rho^* \quad (40a)$$

Alternatively, Eq. (40a) can be cast into the form

$$(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) = [a']^{-\frac{1}{2}} \sum_\rho \langle \tau'a' || T^b || \tau a \rangle_\rho (ab\alpha\beta|\rho a'\alpha')^* \quad (40b)$$

with

$$\langle \tau'a' || T^b || \tau a \rangle_\rho = \sum_{\rho'} M(ab, a')_{\rho\rho'}^* \langle \tau'a' || T^b || \tau a \rangle_{\rho'} \quad (40ab)$$

where  $M(ab, a')$  is an arbitrary unitary matrix (cf., (24) and (25)).

In the summation-factorization afforded by (40), there are two types of terms, namely, the  $(3-a\alpha)_\rho$  symbols or the CGc's  $(ab\alpha\beta|\rho a'\alpha')$  that depend on the group  $G$  only and the so-called reduced matrix elements  $(\tau'a' || T^b || \tau a)_\rho$  or  $\langle \tau'a' || T^b || \tau a \rangle_\rho$  that depend both on  $G$  and on the physics of the problem under consideration. The reduced matrix elements do not depend on the 'magnetic quantum numbers' ( $\alpha'$ ,  $\beta$  and  $\alpha$ ) and therefore, like the recoupling coefficients, are basis-independent. We then understand the interest of the recoupling coefficients in applications : The reduced matrix elements for a composed system may be developed as functions of reduced matrix elements for elementary systems and recoupling coefficients. In this direction, it can be verified that the matrix element  $(\tau_a'\tau_b'a'b'\rho'c'\gamma'|\{T^d \otimes U^e\}_\varphi^{\sigma f}|\tau_a\tau_b ab\rho c\gamma)$  can be expressed in terms of the recoupling coefficients defined by (32) and (34).

Equations (40) generalize the Wigner-Eckart theorem originally derived by Eckart for vector operators of the rotation group [2], by Wigner for tensor

operators of the rotation group [3] and of simply reducible groups [5], and by Racah for tensor operators of the rotation group [7].

A useful selection rule on the matrix element  $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha)$  immediately follows from the CGc's in (40b). The latter matrix element vanishes if the direct product  $a \otimes b$  does not contain  $a'$ . Consequently, in order to have  $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) \neq 0$ , it is necessary (but not sufficient in general) that the IRC  $a'$  be contained in  $a \otimes b$ .

As an interesting particular case, let us consider the situation where  $b$  is the identity IRC 0 of  $G$ . This means that the operator  $H = T_0^0$  is invariant under  $G$  (see Eq. (37)). Equation (40b) can be particularized to

$$(\tau'a'\alpha'|H|\tau a\alpha) = \delta(a'a)\delta(\alpha'\alpha)\langle\tau'a||T^0||\tau a\rangle \quad (41)$$

where the index  $\rho$  is not necessary since  $a \otimes 0 = a$ . The Kroneker deltas in (41) show that there are no  $a'$ - $a$  and/or  $\alpha'$ - $\alpha$  mixing. We say that  $a$  and  $\alpha$  are 'good quantum numbers' for  $H$ . The initial and final states have the same quantum numbers as far as these numbers are associated to the invariance group  $G$ . The invariant  $H$  does not mix state vectors belonging to different irreducible representations  $a$  and  $a'$ . Furthermore, it does not mix state vectors belonging to the same irreducible representation  $a$  but having different labels  $\alpha$  and  $\alpha'$ .

It is important to realize that no phase factors of the type  $(-1)^a$ ,  $(-1)^{a-\alpha}$  and  $(-1)^{a+b+c}$  appear in (40). Indeed, the present exposure is entirely free of such phase factors, in contrast with other works. As a matter of fact, in many works the passage from the Clebsh-Gordan or unsymmetrical form to the  $(3-a\alpha)_\rho$  or symmetrical form of the coupling coefficients involves unpleasant questions of phase. This is not the case in (24) and (25). Such a fact does not mean that (24) and (25) as well as other general relations are free of arbitrary phase factors. In fact, all the phase factors are implicitly contained in the matrices  $M$ , the  $2-a\alpha$  symbols and the (basis-independent) Frobenius-Schur coefficient.

## 4.8 The Racah lemma

We have already emphasized the interest of considering chains of groups rather than isolated groups. Let  $K$  be a subgroup of  $G$ . In this case, the labels of type  $\alpha$  that occur in what preceeds, may be replaced by triplets of type  $\alpha\Gamma\gamma$ . The label of type  $\Gamma$  stands for an IRC of the group  $K$ , the label of type  $\gamma$  is absolutely necessary when  $[\Gamma] > 1$  and the label of type  $\alpha$  is now a branching multiplicity label to be used when the IRC  $\Gamma$  of  $K$  is contained several times in the IRC  $a$  of the head group  $G$ . (The label  $\gamma$  is an internal multiplicity label

for  $K$  and the label  $a$  is an external multiplicity label inherent to the restriction  $G \rightarrow K$ .) Then, the CGc  $(a_1 a_2 \alpha_1 \alpha_2 | \rho a \alpha)$  for the group  $G$  is replaced by the CGc  $(a_1 a_2 \alpha_1 \Gamma_1 \gamma_1 \alpha_2 \Gamma_2 \gamma_2 | \rho a \alpha \Gamma \gamma)$  for the group  $G$  in a  $G \supset K$  basis. We can prove the following theorem.

**Theorem 4** (Racah’s lemma). The CGc’s of the group  $G$  in a  $G \supset K$  basis can be developed according to

$$(a_1 a_2 \alpha_1 \Gamma_1 \gamma_1 \alpha_2 \Gamma_2 \gamma_2 | \rho a \alpha \Gamma \gamma) = \sum_{\beta} (\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \beta \Gamma \gamma) (a_1 \alpha_1 \Gamma_1 + a_2 \alpha_2 \Gamma_2 | \rho a \alpha \Gamma)_{\beta} \quad (40c)$$

where the coefficients  $(\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \beta \Gamma \gamma)$  are CGc’s for the group  $K$  as considered as an isolated group and the coefficients  $(a_1 \alpha_1 \Gamma_1 + a_2 \alpha_2 \Gamma_2 | \rho a \alpha \Gamma)_{\beta}$  do not depend on  $\gamma_1$ ,  $\gamma_2$  and  $\gamma$ .

The proof of Racah’s lemma was originally obtained from Schur’s lemma [7]. However, the analogy between (40a), (40b) and (40c) should be noted. Hence, the Racah lemma for a chain  $G \supset K$  may be derived from the Wigner-Eckart theorem, for the group  $G$  in a  $G \supset K$  basis, applied to the Wigner operator, i.e., the operator whose matrix elements are the CGc’s. The expansion coefficients  $(a_1 \alpha_1 \Gamma_1 + a_2 \alpha_2 \Gamma_2 | \rho a \alpha \Gamma)_{\beta}$  in the development (40c) are sometimes named isoscalar factors, a terminology that comes from the chain  $SU(3) \supset SU(2)$  used in the eightfold way model of subatomic physics.

From a purely group-theoretical point of view, it is worth to note that Racah’s lemma enables us to calculate the CGc’s of the subgroup  $K$  of  $G$  when the ones of the group  $G$  are known [10]. In particular, for those triplets  $(\Gamma_1 \Gamma_2 \Gamma)$  for which  $\Gamma_1 \otimes \Gamma_2$  contains  $\Gamma$  only once, the CGc’s  $(\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \Gamma \gamma)$  are given by a simple formula in terms of the CGc’s of  $G$ .

The summation-factorisation in (40c) can be applied to each CGc entering the definition of any recoupling coefficient for the group  $G$ . Therefore, the recoupling coefficients for  $G$  can be developed in terms of the recoupling coefficients for its subgroup  $K$  [10].

## 4.9 The rotation group

As an illustrative example, we now consider the universal covering group or, in the terminology of molecular physics, the ‘doubled’ group  $SU(2)$  of the proper rotation group  $R(3)$ . In this case,  $a \equiv j$  is either an integer (for vector representations) or a half-an-odd integer (for spinor representations),  $\alpha \equiv m$  ranges from  $-j$  to  $j$  by unit step, and  $\mathcal{D}^a(R)_{\alpha\alpha'}$  identifies to the element  $\mathcal{D}^{(j)}(R)_{mm'}$  of the well-known Wigner rotation matrix of dimension  $[j] \equiv 2j+1$ . The matrix repre-



sentation  $\mathcal{D}^{(j)}$  corresponds to the standard basis  $\{|jm\rangle : m = -j, -j+1, \dots, j\}$  where  $|jm\rangle$  denotes an eigenvector of the (generalized) angular momentum operators  $J^2$  and  $J_z$ . (For  $j$  integer, the label  $\ell$  often replaces  $j$ .) The labels of type  $m$  clearly refer to IRC's of the rotation group  $C_\infty \sim R(2)$ . Therefore, the basis  $\{|jm\rangle : m = -j, -j+1, \dots, j\}$  is called and  $R(3) \supset R(2)$  or  $SU(2) \supset U(1)$  basis. Furthermore, the multiplicity label  $\rho$  is not necessary since  $SU(2)$  is multiplicity-free. Consequently, the (real) CGc's of  $SU(2)$  in a  $SU(2) \supset U(1)$  basis are written  $(j_1 j_2 m_1 m_2 | jm)$ . They are also called Wigner coefficients.

In view of the ambivalent nature of  $SU(2)$ , the 2- $a\alpha$  symbol reduces to

$$\begin{pmatrix} j & j' \\ m & m' \end{pmatrix} = (-1)^{j+m} \delta(j'j) \delta(m', -m) \quad (42)$$

where  $(-1)^{j+m} \delta(m', -m)$  corresponds to the  $1-jm$  Herring-Wigner metric tensor. Then, the introduction of (42) into (24) for the chain  $SU(2) \supset U(1)$  shows that the 3- $a\alpha$  symbol identifies to the 3- $j m$  Wigner symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (2j_3 + 1)^{-\frac{1}{2}} (-1)^{j_3 - m_3 - 2j_2} (j_2 j_1 m_2 m_1 | j_3, -m_3) \quad (43)$$

provided we chose  $M(j_2 j_1, j_3) = (-1)^{2j_1}$ . Such a choice ensures that the 3- $j m$  symbol is highly symmetrical under permutation of its columns.

In the  $SU(2)$  case, the  $(6-a)_{4\rho}$  and  $(9-a)_{6\rho}$  symbols may be chosen to coincide with the 6- $j$  Wigner (or  $\bar{W}$  Fano-Racah) symbol and the 9- $j$  Wigner (or  $X$  Fano-Racah) symbol, respectively. More precisely, we may take

$$\begin{aligned} \left\{ \begin{matrix} j_1 & j_{23} & j \\ j_3 & j_{12} & j_2 \end{matrix} \right\} &= (-1)^{j_1 + j_2 + j_3 + j} [(2j_{12} + 1)(2j_{23} + 1)]^{-\frac{1}{2}} \\ &\times (j_1(j_2 j_3) j_{23} j m | (j_1 j_2) j_{12} j_3 j m) \end{aligned} \quad (44)$$

and

$$\begin{aligned} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{matrix} \right\} &= [(2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)]^{-\frac{1}{2}} \\ &\times ((j_1 j_3) j_{13} (j_2 j_4) j_{24} j m | (j_1 j_2) j_{12} (j_3 j_4) j_{34} j m) \end{aligned} \quad (45)$$

in terms of recoupling coefficients (cf., (33) and (34)).

Finally, for  $a \equiv k$ , the ITS  $\mathbf{T}^a$  coincides with the irreducible tensor operator  $\mathbf{T}^{(k)}$  of rank  $k$  (and having  $2k+1$  components) introduced by Racah. We denote by  $T_q^{(k)}$  the  $SU(2) \supset U(1)$  components of  $\mathbf{T}^{(k)}$ .

All the relations of subsections 4.1-4.7 may be rewritten as familiar relations of angular momentum theory owing to the just described correspondence rules. For example, Eqs. (17) or (18) and (40a) can be specialized to

$$\mathcal{D}^{(j)}(R)_{mm'}^* = (-1)^{m-m'} \mathcal{D}^{(j)}(R)_{-m,-m'} \quad (46)$$

and

$$(\tau' j' m' | T_q^{(k)} | \tau j m) = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} (\tau' j' || T^{(k)} || \tau j) \quad (47)$$

respectively.

## 5 Applications

There exists a huge literature on the application of symmetries considerations to physics. See for instance Refs. [3,7,11] for atomic physics, Refs. [8-10,13] for molecular and condensed matter physics and Refs. [12,13] for nuclear physics. It is not feasible to give here a detailed account of all possible applications. Thus, we limit ourselves to a list of important points for dealing with the applications.

**Degeneracies.** The minimal degeneracies for the eigenvalues of an operator  $H$  invariant under a group  $G$  can be predicted prior to any calculation. They correspond to the dimensions of the irreducible representations of  $G$ . The explanation of the accidental (with respect to  $G$ ) degeneracies of  $H$ , if any, lies on the existence of a larger invariance group.

**State labelling.** The eigenvalues (e.g., energy levels or masses) of an operator (e.g., Hamiltonian or mass operator)  $H$  invariant under a group  $G$  can be classified with the help of the irreducible representations of a chain of groups involving the symmetry or invariance group  $G$ . The eigenvectors (state vectors or wavefunctions) of  $H$  can be also classified or labelled with irreducible representations of the groups of the chain.

**Operator labelling.** For a given physical system, the interactions (involving the Hamiltonian) can be classified according to their transformation properties under a chain of groups. Such a classification is a pre-requisite for the application of the Wigner-Eckart theorem. The queue group in the chain generally corresponds to an actual (or idealized) symmetry and the other groups to approximate symmetries and/or classification groups. If the interactions are known the chain can be derived by inspection. On the other hand, if the interactions are postulated, the chain follows from physical and mathematical arguments. In this case, the Hamiltonian for the system is written as a linear combination of operators invariant under the various groups of the chain. The coefficients of the linear combination are phenomenological parameters to be fitted

to experimental data and interpreted in the framework of (microscopic) models. Along this vein, we can quote the Iachello-Levine vibron model based on the chains  $U(4) \supset SO(4) \supset SO(3) \supset SO(2)$  and  $U(4) \supset U(3) \supset SO(3) \supset SO(2)$  for diatomic molecules [13]. Let us also mention the Arima-Iachello interacting boson model (IBM) and the interacting boson-fermion model in nuclear structure physics [12,13]. The three chains  $U(6) \supset U(5) \supset SO(5) \supset SO(3)$ ,  $U(6) \supset SO(6) \supset SO(5) \supset SO(3)$  and  $U(6) \supset SU(3) \supset SO(3)$  are used in the IBM ; they correspond to three different regimes.

**Level splitting.** The splitting of the spectrum of an operator  $H_0$  invariant under a group  $G_0$  when we pass, in a perturbative or nonperturbative way, from  $H_0$  to  $H_0 + H_1$ , where  $H_1$  is invariant under a subgroup  $G_1$  of  $G_0$ , can be determined by studying the restriction  $G_0 \rightarrow G_1$ . Familiar examples concern the Zeeman effect, the (homogeneous) Stark effect, and the crystal- and ligand-field effects.<sup>7</sup>

More quantitative applications concern : (i) The effective determination of symmetry adapted vectors (e.g., normal vibration modes of a molecule, symmetry adapted functions like molecular orbitals in the framework of the linear combination of atomic orbitals (LCAO) method,  $N$ -particle wavefunctions) ; (ii) The factorization of the secular equation ; (iii) The determination of selection rules. We briefly discuss in turn these points.

**Normal modes.** The determination of the normal vibration modes of a molecule or complex ion or small aggregate goes back (with the theory of level splitting for ions in crystals) to the end of the twenties. It is based on the reduction of a representation arising from the transformation properties of the molecular skeleton.

**Symmetry adapted functions.** In general, functions (e.g., atomic and nuclear wavefunctions, molecular orbitals, etc.) can be obtained from the method of projection operators developed by, among others, Wigner, Löwdin and Shapiro. This is sometimes referred to as the Van Vleck generating machine : The action on an arbitrary function of a projection operator associated to an irreducible representation  $\Gamma$  of a group  $G$  produces nothing or a function transforming according to  $\Gamma$ . One then easily understands why the atomic orbitals occurring in a LCAO molecular orbital have the same symmetry. This fact illustrates a general characteristic when dealing with symmetries : A mixing between state vectors of different symmetries with respect to a group  $G$  can

---

<sup>7</sup>Crystal- and ligand-field theories are standard tools for analyzing thermal, optical and magnetic properties of transition elements ( $nd^N$  and  $nf^N$  ions) in crystals [8-10].

be performed only owing to a transition operator which is not invariant under  $G$ .

**$N$ -particle wavefunctions.** The concepts of seniority and coefficients of fractional parentage (cfp's) introduced by Racah [7] provides us with an alternative to the determinantal Slater method. The wavefunctions for a system of  $N$  equivalent particles (nucleons or electrons) can be developed in terms of the wavefunctions for a subsystem of  $N - 1$  particles. The expansion coefficients involve cfp's which can be thought of Clebsch-Gordan coefficients for a chain of groups. These Clebsch-Gordan coefficients can be factorized according to Racah's lemma.

**Secular equation.** A cornerstone for the application of group theory to physics is the Wigner-Eckart theorem in its generalized form that allows one to calculate matrix elements and to build secular equations (energy matrices or mass matrices). Since it is not possible to admix, via an operator invariant  $H$  under a group  $G$ , wavefunctions belonging to different irreducible representations of  $G$  (cf., Eq. (41)), a secular equation for  $H$  can be factorized into blocks corresponding to distinct irreducible representations of  $G$ .

**Selection rules.** Such rules already occur in the determination of matrix elements. They are particularly useful in the determination of intensities  $|\Sigma(f\Gamma_f\gamma_f|T_\gamma^\Gamma|i\Gamma_i\gamma_i)|^2$  for the transitions induced by a tensor operator  $\mathbf{T}^\Gamma$  between an initial state  $i$  and a final state  $f$ .

To summarize this paper, we have shown how symmetries occur in nuclear, atomic, molecular and (to some extent) condensed matter physics through the introduction of groups and chains of groups. Such chains involve symmetry and classification groups. Group theory is thus an important tool for classification purposes by means of 'boxes' constituted by irreducible representations of groups. The classification may concern wavefunctions and interactions.<sup>8</sup> We have also examined how the Wigner-Racah algebra associated to a chain of groups provides us with a useful tool for calculating quantum-mechanical matrix elements. To close, let us mention that other structures (more specifically, graded Lie groups, graded Lie algebras, quantum groups and Hopf algebras) are in the present days the object of an intense activity in connection with 'new symmetries' (as, for example, supersymmetries).

---

<sup>8</sup>To be complete, the classification may also concern atomic and subatomic particles (cf., the group  $SU(3)$  for the three light flavors of quark and the group  $SU(2)\otimes SO(4,2)$  for the periodic table of chemical elements) as well as fields (e.g., the matter and gauge fields of the  $SU(3)_c\otimes SU(2)_L\otimes U(1)_Y \supset SU(3)_c\otimes U(1)_Q$  standard model of particle physics).

## Appendix : Note on the Hydrogen Atom

Let us start with the Hamiltonian  $H$  for a three-dimensional hydrogenlike atom (see Eq. (0) of Example 9). (Equation (0)) follows after separation of the collective and electronic motions. The units are such that  $e = \hbar = 1$  and the reduced mass electron-nucleus is taken to be equal to 1.) In Eq. (0), we take

$$\Delta = \sum_{a=1}^3 \frac{\partial^2}{\partial x_a^2} \quad r = \sqrt{\sum_{a=1}^3 x_a^2}$$

The components  $L_a$  with  $a = 1, 2, 3$  of the angular momentum of the electron can be written as

$$L_a = \frac{1}{2} \varepsilon_{abc} L_{bc} \quad \text{where} \quad L_{ab} = x_a p_b - x_b p_a \quad \text{and} \quad p_a = -i \frac{\partial}{\partial x_a}$$

We know that the observables  $L_a$  with  $a = 1, 2, 3$  and  $L^2 = \sum_{a=1}^3 L_a^2$  are constants of motion since

$$[L^2, H] = [L_a, H] = 0 \quad a = 1, 2, 3$$

Other constants of the motion are provided by the Runge-Lenz-Pauli vector<sup>9</sup>  $\vec{M}(M_1, M_2, M_3)$  defined by

$$\vec{M} = -Z \frac{\vec{r}}{r} + \frac{1}{2} (\vec{p} \times \vec{L} - \vec{L} \times \vec{p})$$

in terms of the vectors  $\vec{p}(p_1, p_2, p_3)$  and  $\vec{L}(L_1, L_2, L_3)$ . We can check that

$$[M^2, H] = [M_a, H] = 0 \quad a = 1, 2, 3$$

where  $M^2 = \sum_{a=1}^3 M_a^2$ .

We now ask the question : What becomes the Lie algebra  $\mathfrak{so}(3)$  (of the group  $\text{SO}(3)$ ), spanned by the operators  $L_a$ , when we introduce the operators  $M_a$  ? In this respect, we have the following commutation relations

$$[L_a, L_b] = i \varepsilon_{abc} L_c \quad [L_a, M_b] = i \varepsilon_{abc} M_c \quad [M_a, M_b] = i(-2H) \varepsilon_{abc} L_c \quad (\text{A.1})$$

Equations (A.1) do not define a Lie algebra due to the presence of the operator  $H$  that prevents  $[M_a, M_b]$  to be a linear combination of the  $L_a$ 's and  $M_a$ 's. In addition to (A.1), we can show that

$$\sum_{a=1}^3 L_a M_a = \sum_{a=1}^3 M_a L_a = 0 \quad M^2 - Z^2 = 2H(L^2 + 1) \quad (\text{A.2})$$

---

<sup>9</sup>It is the quantum-mechanical analogue of the Laplace-Runge-Lenz vector well known in classical mechanics.

From Eqs. (A.1) and (A.2), it is possible to construct an infinite dimensional Lie algebra or even a finite  $W$  algebra. We shall not do it here. We shall rather consider (A.1) for the various parts (discrete, continuous and zero-energy point) of the spectrum of  $H$ .

1. For the discrete spectrum, we have  $H < 0$  in (A.1) and we introduce

$$A_a = \sqrt{-\frac{1}{2H}} M_a \quad J_a = \frac{1}{2}(L_a + A_a) \quad K_a = \frac{1}{2}(L_a - A_a) \quad a = 1, 2, 3$$

This leads to

$$[J_a, J_b] = i\varepsilon_{abc} J_c \quad [K_a, K_b] = i\varepsilon_{abc} K_c \quad [J_a, K_b] = 0$$

which is reminiscent of the six-dimensional Lie algebra  $\mathfrak{so}(4)$  of the group  $\text{SO}(4)$  in an  $\mathfrak{so}(3) \oplus \mathfrak{so}(3)$  basis. It is clear that the generators of  $\text{SO}(4)$  commute with  $H$ , a fact that ensures that  $H$  is invariant under  $\text{SO}(4)$ .

The discrete energy spectrum then follows from (A.2) and the quantization of  $\{J^2 = \sum_{a=1}^3 J_a^2, J_3\}$  and  $\{K^2 = \sum_{a=1}^3 K_a^2, K_3\}$ . The first constraint relation (A.2) yields  $J^2 = K^2$ . Let  $j(j+1)$  with  $2j \in \mathbf{N}$  be the common eigenvalues of  $J^2$  and  $K^2$ . Then, by introducing  $J^2 = K^2 = j(j+1)$  and  $H = E$  in the second constraint relation (A.2), we arrive at the familiar result

$$E \equiv E_n = -\frac{1}{2} \frac{Z^2}{n^2} \quad n = 2j + 1 \in N^*$$

The degree of degeneracy of  $E_n$ , namely  $(2j+1)(2j+1) = n^2$ , is obtained by counting the number of states arising from a subspace of eigenvectors, associated to the quantum number  $j$ , of the two commuting sets of operators  $\{J^2, J_3\}$  and  $\{K^2, K_3\}$ . In conclusion, the level  $E_n$  is linked to the irreducible representation  $(j, j)$ , with  $j = (n-1)/2$ , of  $\text{SO}(4)$ .

2. For the continuous spectrum, we have  $H > 0$  in (A.1) and we put

$$B_a = \sqrt{\frac{1}{2H}} M_a \quad a = 1, 2, 3$$

This leads to

$$[L_a, L_b] = i\varepsilon_{abc} L_c \quad [L_a, B_b] = i\varepsilon_{abc} B_c \quad [B_a, B_b] = -i\varepsilon_{abc} L_c$$

which corresponds to the Lie algebra  $\mathfrak{so}(3,1)$  of the group  $\text{SO}(3,1)$ .

3. For the zero-energy point, we have  $H = 0$  in (A.1). We thus obtain

$$[L_a, L_b] = i\varepsilon_{abc} L_c \quad [L_a, M_b] = i\varepsilon_{abc} M_c \quad [M_a, M_b] = 0$$

which defines the Lie algebra  $\mathfrak{e}(3)$  of the Euclidean group  $\text{E}(3)$ .

## References

- [1] E.P. Wigner, Z. Physik **43**, 624 (1927).
- [2] C. Eckart, Rev. Mod. Phys. **2**, 305 (1930).
- [3] E.P. Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren* (Vieweg, Braunschweig, 1931).
- [4] E.P. Wigner, Am. J. Math. **63**, 57 (1941).
- [5] E.P. Wigner, manuscript from 1940 published in *Quantum Theory of Angular Momentum*, eds., L.C. Biedenharn and H. van Dam (Academic, New York, 1965).
- [6] E.P. Wigner, in *Spectroscopic and Group Theoretical Methods in Physics*, eds., F. Bloch *et al.* (North-Holland, Amsterdam, 1968).
- [7] G. Racah, Phys. Rev. **61**, 186 (1942) ; **62**, 438 (1942) ; **63**, 367 (1943) ; **76**, 1352 (1949).
- [8] J.S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups* (Prentice-Hall, Englewood Cliffs, NJ, 1962).
- [9] S. Sugano, Y. Tanabe and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).
- [10] M. Kibler, in *Recent Advances in Group Theory and Their Application to Spectroscopy*, ed., J.C. Donini (Plenum, New York, 1979) ; *Eléments de théorie des groupes* (IPN de Lyon, 1982) ; Int. J. Quantum Chem. **23**, 115 (1983) ; Croat. Chem. Acta **57**, 1075 (1984).
- [11] E.U. Condon and H. Odabaşı, *Atomic Structure* (Cambridge Univ. Press, Cambridge, 1980).
- [12] F. Iachello and A. Arima, *The Interacting Boson Model* (Cambridge Univ. Press, Cambridge, 1987).
- [13] A. Frank and P. Van Isacker, *Algebraic Methods in Molecular and Nuclear Structure Physics* (John Wiley, New York, 1994).